

## ANALYSIS OF DURABILITY IN LITHIUM NICKEL OXIDE ELECTROCHROMIC MATERIALS AND DEVICES

S-J. Wen, J. Kerr, M. Rubin, J. Slack, K. von Rottkay

Lawrence Berkeley National Laboratory  
Mail Stop 2-300, University of California, Berkeley, CA 94720 USA  
Tel: 510-486-7124, Fax: 510-486-6099, E-Mail: MDRubin@lbl.gov

### Abstract

Thin films of lithium nickel oxide were deposited by sputtering and laser ablation from targets of pressed nickel oxide and lithium oxide powders. These films were assembled into electrochromic test devices with tungsten oxide as the opposite electrode and a polymer electrolyte. Analysis of the failure modes was carried out at several levels: The composition and structure of the films were examined before and after cycling using a variety of techniques, such as infrared spectroscopy, nuclear-reaction analysis, Rutherford backscattering spectrometry, x-ray diffraction and atomic force microscopy. Absorption of water vapor was found to be a major factor determining the cyclic stability of the films. A new technique is described for incorporating reference electrodes made from an electronically isolated corner into devices. This structure enabled identification of potential problems associated with a particular interface. Finally, some of the devices were disassembled and the components examined. For example, a small quantity of the polymer was extracted and studied by gas chromatography and mass spectroscopy. Small organic fragments were discovered which correspond to expected weak points in the polymer structures.

### Introduction

The most straightforward method to test the durability of electrochromic devices is to expose them to real or simulated environmental conditions with electrical/optical cycling. In this way, accelerated testing techniques could eventually be developed to reliably predict real-time effects. Testing and analysis of durability for electrochromic devices is a very complex problem involving many variables as discussed by Czanderna.<sup>1</sup> Furthermore, the electrical testing process is inherently time consuming even under accelerated conditions. The nature of the problem calls for the use of innovative diagnostic techniques that will allow us to identify the degradation mechanisms and predict failure in the early stages. Components tested in isolation will often behave differently than in the environment of a device, either better or worse. Nevertheless, the behavior of a new component material, when compared to that of the final device can be instructive.

The first example of degradation analysis in this paper will attempt to correlate the hygroscopic tendencies of a new form of lithium nickel oxide to device performance. Another technique that has the potential to give much more detailed information about the

internal processes in electrochromic devices in general is the use of reference electrodes. Size limitations have prevented the introduction of reference electrodes in the study of thin-film electrochromic devices despite their universal usage in standard electrochemical tests and even in experiments on bulk batteries. In this paper, we describe a technique for fabrication of internal reference electrodes and demonstrate their value. Destructive analysis of electrochromic devices is a powerful means of studying the internal changes in device components. Devices made using polymer electrolytes can be easy to fabricate as well as to dismantle. Analysis of the thin-film electrodes and conductors then becomes possible by a variety of surface and bulk techniques. In this paper, we report on analysis of the polymer itself by gas chromatography supplemented with mass spectroscopy.

### Stability of $\text{Li}_x\text{Ni}_{1-x}\text{O}$

Recently, we developed a new form of lithium nickel oxide  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  by pulsed laser deposition (PLD).<sup>2</sup> Since then we have duplicated the films using sputtering. Devices were constructed primarily as test packages for the  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  material using otherwise well known components: ITO transparent conductors,  $\text{WO}_3$  electrode, and PEO polymer electrolyte. We summarize some of the features of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  here.

Nickel oxide thin films deposited by sputtering are face-centered cubic with the NaCl structure near the stoichiometric composition NiO. Electrochemical cycling of NiO was found to result in an irreversible uptake of lithium on vacant nickel sites.<sup>3</sup> This stable lithium compound then can reversibly intercalate a further quantity of lithium accompanied by an electrochromic coloration effect. It was later observed that superior films could be obtained by directly incorporating Li into the film structure during the sputter deposition.<sup>4</sup> Such films required less formatting, switched over a wider optical range and had better stability. Those films, however, were still not fully stoichiometric  $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$  as deposited.

Cyclic voltammograms were obtained from fresh PLD and sputtered films. The films were cycled in 1M  $\text{LiPF}_6$  in 1:1 ethylene carbonate/propylene carbonate over the range 1.0 to 4.5 V vs.  $\text{Li/Li}^+$  using lithium foil counter and reference electrodes. While the initial open circuit potentials of the two films were nearly the same, their electrochemical behavior was quite different. The stoichiometric  $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$  PLD film (Figure 1a) was very stable over eight cycles and achieved its full optical range on the first cycle. Both the optical and electrochemical behavior are very similar to that achieved with slightly substoichiometric sputtered films after 123 cycles<sup>4</sup>. We also tested a sputtered film that was far from stoichiometric composition at  $\text{Li}_{0.09}\text{Ni}_{0.25}\text{O}_{0.66}$  (Figure 1b). The electrochromic behavior of this sputtered film strongly resembles that of  $\text{Li}_x\text{NiO}_2$  powder<sup>5</sup>. The optical range is much narrower and unstable. It shows the bimodal transmittance characteristic discovered by Passerini and Scrosati<sup>6</sup> for formatted NiO films, i.e., the transmittance eventually turns down as more charge is injected. After a full cycle the transmittance recovers its maximum level.

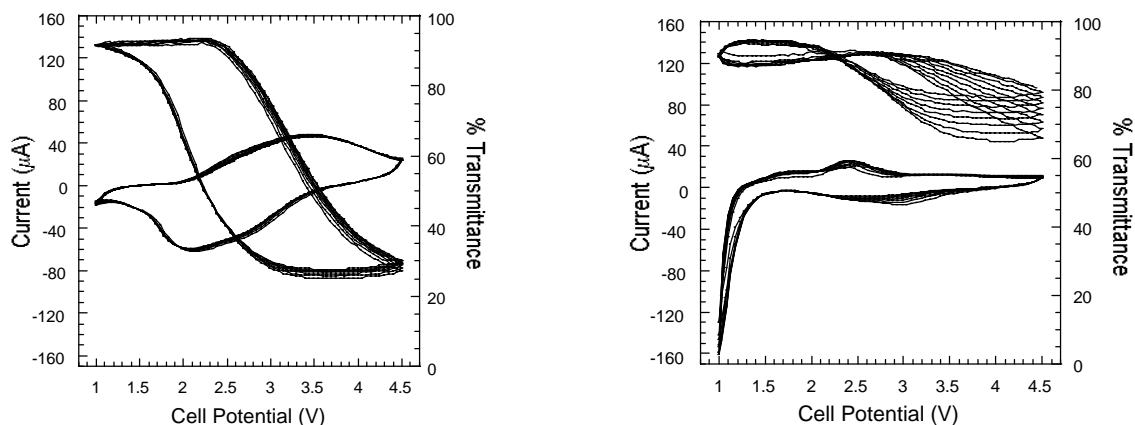


Figure 1. Cyclic voltammograms and transmittance/voltage of: a) PLD  $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$  and b) sputtered  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ .

Films deposited at room temperature were found to be amorphous by x-ray diffraction (XRD). Nevertheless, we can get some local structural information on low-temperature films by performing XRD on films deposited at higher temperatures and then comparing to supplementary FTIR data at both high and low temperatures. PLD films deposited at  $400\text{ }^\circ\text{C}$  or  $600\text{ }^\circ\text{C}$  show a cubic structure corresponding to  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ . FTIR spectra of PLD films deposited at room temperature have the same Ni-O (or Li-O) absorption bands as those of the PLD film deposited at elevated temperatures of  $400\text{ }^\circ\text{C}$  or  $600\text{ }^\circ\text{C}$  (see Figure 2). The low-temperature films, however, are sensitive to the atmosphere, showing absorption bands of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  not present in the high-temperature films. This phenomenon is very similar to the case of  $\text{NiO}$ .<sup>7,8</sup> The films deposited at  $600\text{ }^\circ\text{C}$  proved to be stable in air over a long period. FTIR spectra of room-temperature sputtered films with lithium deficiency show similar absorption bands as those of PLD films but slightly shifted. Sputtered films also show surface sensitivity to the air but with higher activity. The greatly different composition of the sputtered films and appearance of a double peak possibly indicate the formation of a second phase.

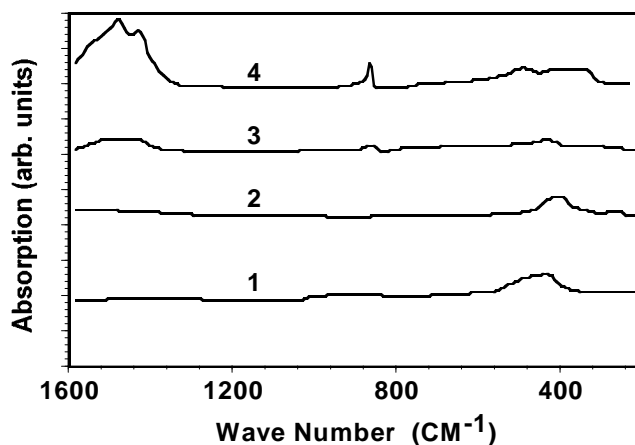


Figure 2 FTIR Powder and Films: 1) powder  $\text{NiO}$  2) PLD  $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$  ( $600\text{ }^\circ\text{C}$ ) 3) PLD  $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$  (r.t.) 4) sputtered  $\text{Li}_{0.1}\text{Ni}_{0.3}\text{O}_{0.6}$

Films that have been measured by FTIR and XRD are exposed to the atmosphere much longer and even the purged FTIR compartment is much less pure than the dry box used for device fabrication. Nevertheless, the tendency for devices to absorb water vapor should be relatively represented by the FTIR. Neither growth method, temperature, or pressure nor film characteristics such as composition or surface roughness are unambiguously correlated with film stability. The parameter that seems to most consistently affect the stability of the of PLD and sputtered films is the tendency to absorb water vapor.

### Reference Electrodes for Nondestructive Testing of Devices

Incorporation of reference electrodes into devices would allow monitoring of internal device potentials.<sup>9</sup> The complementary electrochromic electrodes are  $\text{WO}_3$  and  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ . The solid polymer electrolyte is a capped amorphous PEO/LiTFSI layer with a thickness of 200-250 microns. A more complete description of the polymer is given in the next section. A small area of either electrode and transparent conductor, located at the corner of the device, was isolated electrically from the active area by scribing the film (see Figure 3). This isolated electrode serves as a pseudoreference because it remains in contact with the same electrolyte layer as the active electrodes.. The area of the reference is approximately  $0.1 \times 0.1 \text{ cm}^2$  while the active area of the device is a much larger  $2 \times 2 \text{ cm}^2$ . The isolation gaps are typically 150-200 microns; on the order of the thickness of the polymer.

Electrochemical measurements were performed with an Arbin multichannel potentiostat/galvanostat. This instrument was configured with an auxiliary input/output for each channel to allow for the recording of optical transmittance data. Measurements on films were made inside a dry box at less than 1 ppm of  $\text{O}_2$ . For standard two-terminal devices, one channel with two output/input connections was used to control the experiments, either by fixing the applied voltage between the two electrodes ( $V_1-V_2$ ) or by controlling  $V_1-V_2$  using optical transmission feedback. For devices with built-in reference electrodes (see below), two additional channels were used to simultaneously record the voltage signals  $V_3-V_1$ ,  $V_3-V_2$ ,  $V_4-V_2$  and  $V_4-V_1$  between the four electrodes.

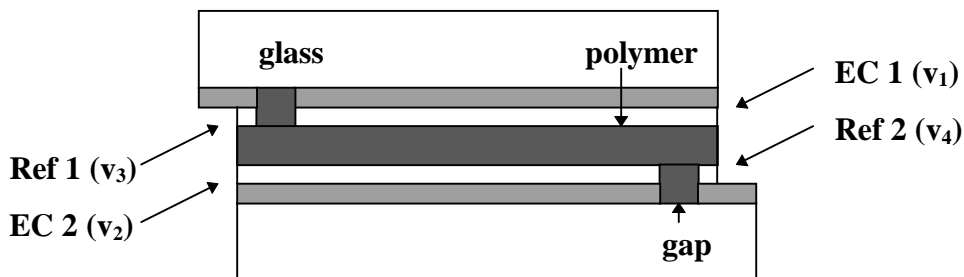


Figure 3 Schematic device with two built-in reference electrodes.

In situ diagnostics of devices built to test these electrodes is greatly aided by the use of devices containing a reference or pseudo-reference electrode. In a 2-terminal device only the voltage applied across the full device is known. The time-dependent voltages that

develop within the device are unknown unless the potentials of the various components can somehow be accessed. Two devices were tested under conditions that resulted in significant degradation of electrochemical and optical properties over thousands of cycles. Deterioration occurs in both bleach/coloration capacity as well as optical transmission. Devices A and B both contain  $\text{WO}_3$  and  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  electrodes, but in device B the  $\text{WO}_3$  layer is thicker and is made under optimal conditions. For device A, coloration capacity is always slightly larger than bleach capacity while the reverse is true for device B. Figure 4a shows that for device A, the polarization ( $V_4-V_2$ ) at the  $\text{WO}_3$ /polymer interface increased with cycling while  $V_4-V_1$  decreased. For device B in Figure 4b, the opposite trend occurred, i.e.  $V_4-V_1$  increased with cycling and  $V_4-V_2$  stayed roughly constant. So, in this case, polarization was increasing at the  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  interface. Some recovery of devices was later possible using feedback control methods.

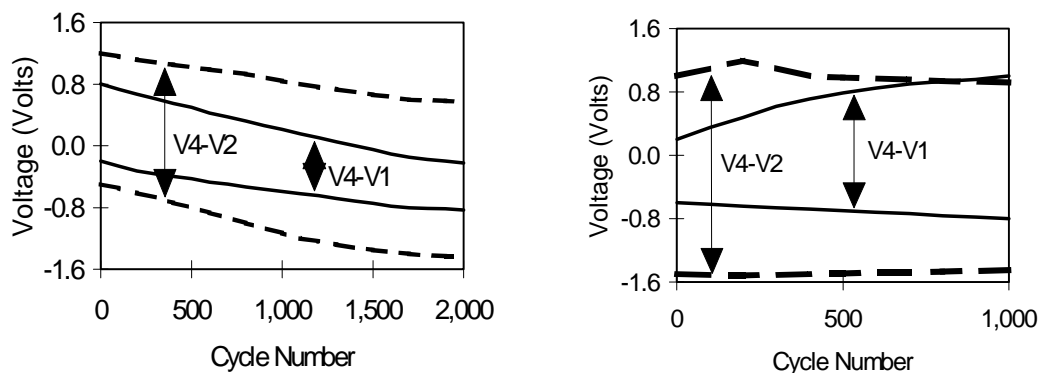


Figure 4. Cycling of devices with reference electrodes: a) device A; b) device B

### Gas Chromatography of Polymers: Destructive Testing of Devices

Some devices were cut apart and the polymers are dissolved off with methylene chloride. We also place the films in water to hydrolyze any insoluble salts and then extract any products into methylene chloride. Usually we then combine the methylene chloride extracts for analysis by gas chromatography. Mass spectroscopy was also used in some cases for unambiguous assignment of peaks. We can keep the aqueous extracts separate from the non-aqueous polymer solutions to see if there are differences due to insoluble layers on the films.

After examination of the internal potentials during cycling, the devices can be dismantled to see, among other things, what has happened to the polymer. The purpose of the methylene link in amorphous PEO polymer is to disrupt the symmetry of the polymer structure and thereby prevent the formation of crystals which impede conductivity. The oxymethylene link, however, may be more vulnerable to cleavage due to UV light or oxidation. One therefore might expect to see a product distribution from degradation that reflects the suspected weakness of this structure.

The chemical reactions that may lead to degradation of a polymer result from ultraviolet and visible radiation and from strongly reducing and oxidizing conditions at the electrode/polymer interfaces. It is also possible that the electrode surface could act as a photocatalyst to initiate chemical reactions in the polymer. The products of these

reactions may build up resistive layers at the electrode surfaces leading to the need for higher voltages to push the lithium ions through the layers into the electrodes. Products could also be formed which intercalate into the electrodes leading to irreversible change in the electrode and consequent failure of the device.

Homolytic cleavage of a carbon-oxygen bond by ultraviolet photons might be an expected reaction. A particularly vulnerable group within a polymer might be a tertiary carbon next to an oxygen or an oxymethylene link where one carbon is connected to two oxygens (see Figure 5).

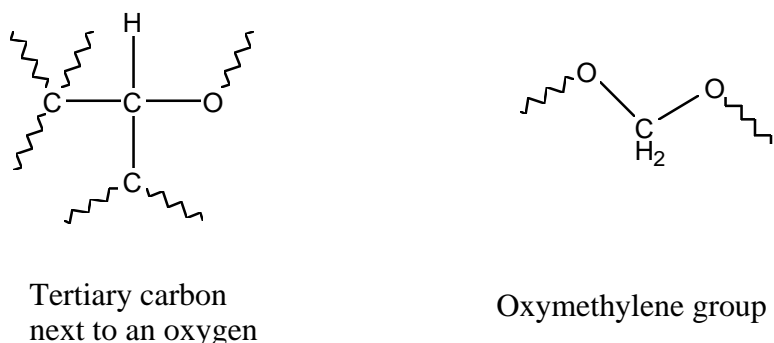


Figure 5. Groups potentially vulnerable to ultraviolet damage.

Reduction of the carbon-oxygen bond by injection of one or more electrons would proceed as diagrammed in Figure 6:

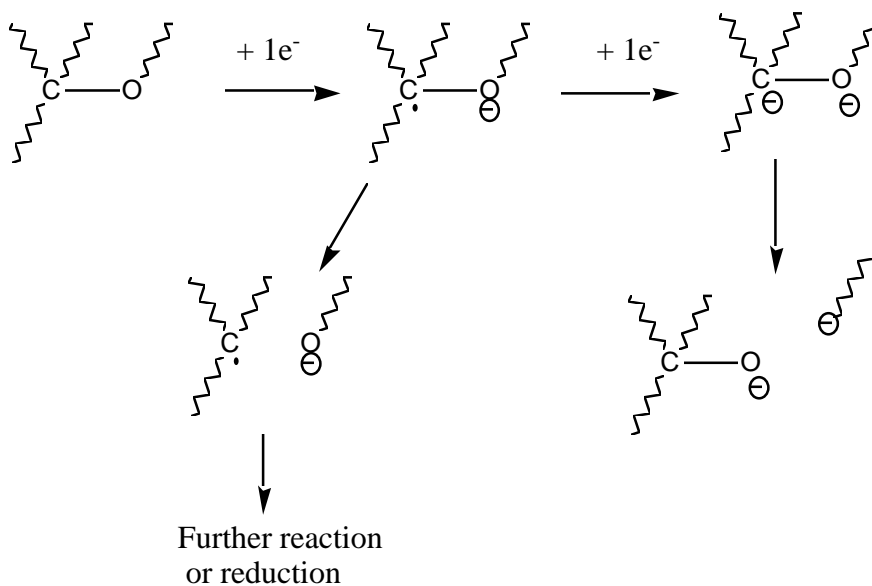


Figure 6. Reduction reaction mechanism

Oxidation of carbon-oxygen bonds by removal of one or more electrons would proceed as diagrammed in Figure 7:

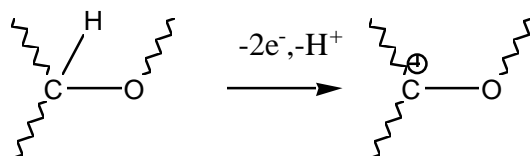


Figure 7. Oxidation reaction mechanism.

These reactions, should they occur, will generate unstable intermediates which are favored or disfavored by various structural features built into the polymers. Thus, from a knowledge of the chemistry and appropriately constructed polymers, one might be able to obtain information about the nature of the degradation process by analysis of the degradation products. The method is quite analogous to that used for sequencing DNA and proteins where the biological polymers are chopped up in order to learn about the structural features and any changes that may have occurred.

The polymer used to prepare our test devices is a variation of PEO called oxymethelene-linked polyethylene glycol or amorphous PEO which is quite conductive at room temperature ( $10^{-5}$  S/cm) with Li Trifluoromethylsulfonfyl imide (LiTFSI) as the electrolyte salt. The polymer electrolyte is completely amorphous exhibiting no crystallinity and a glass transition temperature  $T_g$  of about  $-55^\circ\text{C}$ . The polymer structure is shown in Figure 8.

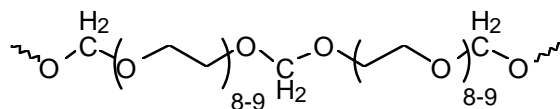


Figure 8. Structure of oxymethelene-linked PEG 400.

Figure 9a. shows the chromatogram of capped PEO/LiTFSI with building blocks of 8 or 9 ethylene oxide units taken from a  $\text{WO}_3/\text{Li}_x\text{Ni}_{1-x}\text{O}$  device after cycling. The largest ethylene oxide product is  $\text{E}_8$  which is  $\text{MeO}-(\text{CH}_2\text{CH}_2\text{O})_8\text{H}$  with a molecular weight of 368 and  $\text{E}_9$  with a molecular weight of 412. The product distribution observed here does reflect a breakage at the oxymethylene linkage. However, the amount of  $\text{E}_3$  formed is anomalous. This device was made with reference electrodes and showed an increasing resistance at the  $\text{WO}_3$  interface as described above. A symmetric device with matching  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  electrodes was tested to eliminate the effect of the  $\text{WO}_3$ . In this case, the results are very similar to the previous asymmetric device, but  $\text{E}_3$  is now of the same magnitude as the surrounding peaks (Figure 9b). The increased level of  $\text{E}_3$  may therefore result from an interaction with the  $\text{WO}_3$ . Analysis of a cycled symmetrical  $\text{WO}_3$  device would now be interesting, but the first devices of this type failed early in testing.

A polymer made with building blocks of 5 ethylene oxide units, rather than 8 units, as in the first two examples, was used for the next device experiment. The chromatogram of this device was taken after only a few initial cycles followed by storage at room temperature for six months. shows high incidence of  $\text{E}_1$  and  $\text{E}_2$ , less strong  $\text{E}_3$ ,  $\text{E}_4$  and  $\text{E}_5$  peaks, and essentially nothing above  $\text{E}_5$  except for small fragments which resulted from

coblen ding. This is practically the reverse trend from the previous cases. The polymer is clearly being broken down thermally and in a very different way from the cycled devices.

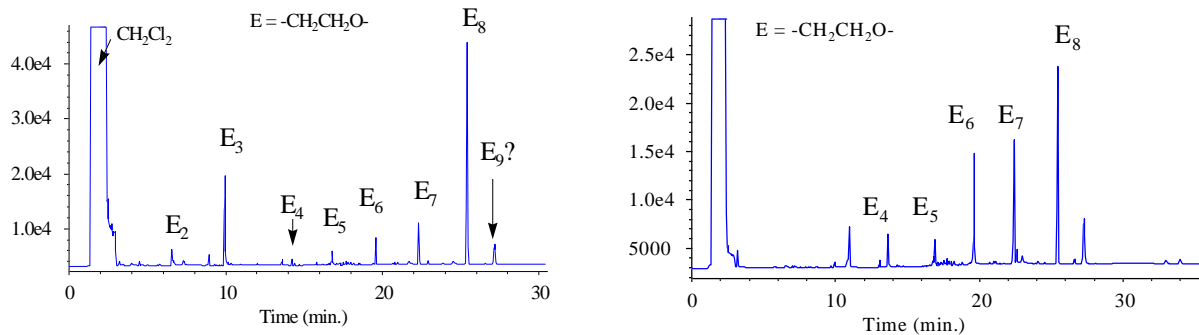


Figure 9. Gas Chromatograms of  $\text{CH}_2\text{Cl}_2$  extracts from two cycled devices: a)  $\text{LiNiO}_x/\text{caPEO-LiTFSI}/\text{WO}_3$  and b)  $\text{LiNiO}_x/\text{caPEO-LiTFSI}/\text{NiO}_x$  cycled symmetrical device.

## Conclusions

Infrared analysis of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  films consistently showed the detrimental effect of water absorption. In electrochromic devices, two methods, one destructive and one nondestructive, were found to be useful for assessing the failure mechanisms. A novel technique for incorporating reference electrodes into thin-film devices helped us to locate interfacial problems. Destructive analysis of the polymer electrolytes by gas chromatography showed polymer degradation and also indicated the electrodes which were the source of the degradation.

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